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Pyrolysis characteristics of bean dregs and in situ visualization of pyrolysis transformation

Guangyong Zhu[a], Xian Zhu[b,*], Zuobing Xiao[a,*], Rujun Zhou[a], Fengping Yi[a]

[a] *Shanghai Institute of Technology, Shanghai 201418, PR China*
[b] *Dept. of Chem. Eng., Shanghai University, Shanghai 200444, PR China*

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ABSTRACT

Biomass is an important renewable and sustainable source of energy. Waste products from biomass are considered as attractive feedstocks for the production of fuel. This work deals with the pyrolysis of bean dregs, a biomass waste from soybean processing industry. A technique has been developed to study bean dregs pyrolysis by in situ visualization of bean dregs transformation in a quartz capillary under a microscope using a charge-coupled device (CCD) camera monitoring system. The technique enables us to observe directly the processes and temperatures of bean dregs transformation during pyrolysis. In situ visualization of reaction revealed that how oily liquids are generated and expulsed concurrently from bean dregs during pyrolysis. Pyrolysis characteristics were investigated under a highly purified N_2 atmosphere using a thermogravimetric analyzer from room temperature to 800 °C at different heating rates of 10, 30 and 50 °C/min. The results showed that three stages appeared in this thermal degradation process. The initial decomposition temperature and the peak shifted towards higher temperature with an increase in heating rate. Kinetic parameters in terms of apparent activation energy and pre-exponential factor were determined.

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1. Introduction

With the depletion of petroleum resource and fossil fuels, it is necessary and urgent that finding alternative and renewable fuels. Because of the global warming problem resulting from combustion of fossil fuels, a lot of efforts are pushing towards the replacement of fossil fuels with alternative energy sources. Due to inexhaustible and potential energetic application of biomaterials, the exploration to effectively utilize this sort of resource is very attractive. Biomass is an important renewable and sustainable source of energy. Since living biomass fixes carbon dioxide from atmosphere during photosynthesis to synthesize hydrocarbon in its structure, combustion of almost all of the fresh or waste biomass species does not cause to any significant contribution to the net carbon dioxide deposition in atmosphere (Haykiri-Acma and Yaman, 2008).

Pyrolysis has been widely used for utilizing biomass materials (Jeguirim and Trouve, 2009; Park et al., 2009a,b; Kumar et al., 2008). Among the various biomass materials, bean dregs are a potential source of energy and value-added products. Bean dregs come from soybean processing industry. Soybean is the main oil-bearing crop and an important food resource. Because soybean has comprehensive and rich nutrients, the soybean processing industries are in the ascendant. More than 80,000 tons wastes of bean dregs, the main by-product of soybean processing industry, are produced annually in recent years in China. However, only a small fraction of bean dregs were used for poultry and livestock feed. Most of them were arbitrarily dumped into fields. Bean dregs consist of cellulose, protein, fat and minor amount of other organics (Jiang and Hu, 2008; Zhu and Zheng, 2004). It is recommended to utilize bean dregs as a source of renewable energy and value-added products, based on both benefits of energy or value-added product recovery and environmental protection.

For the proper design and operation of the pyrolysis conversion systems, a thorough knowledge of the thermal behavior and pyrolysis kinetics of bean dregs are required. Up to now, bean dregs pyrolysis has not been visually investigated. In this paper, we present the visual characteristics of bean dregs during pyrolysis in a quartz capillary. The visual capability of the capillary technique provides direct observations showing how oil is generated and expulsed concurrently from bean dregs during pyrolysis. Thermogravimetric analysis (TGA) was also selected for the thermal decomposition process. The characteristics of the thermal degradation of bean dregs at different heating rates were studied. The kinetic parameters were obtained by Coats–Redfern method (Coats and Redfern, 1964), Kissinger–Akahira–Sunose (KAS) method (Kissinger, 1957) and Flynn–Wall–Ozawa (FWO) method

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* Corresponding authors. Tel./fax: +86 21 66137727 (X. Zhu), +86 21 60873507 (Z. Xiao).
E-mail addresses: gyz@shu.edu.cn (X. Zhu), xzb@sit.edu.cn (Z. Xiao).

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Corresponding authors. Tel./fax: +86 21 66137727 (X. Zhu), +86 21 60873507 (Z. Xiao).(Flynn and Wall, 1966; Ozawa, 1965). The results of this study are very useful in helping us understand the thermal degradation processes and mechanisms, and provide information for designing a pyrolytic processing system using bean dregs as feedstock.

2. Methods

2.1. Material

Bean dregs wastes came from Shanghai University Canteen. Before the experiments, the dried bean dregs were milled for 10 min using a mixer (HR170, Philips Corp.) at the maximum speed setting, and then were further grinded with a high-speed rotary grinder (Pulverisette, Fritsch Corp.) to make even smaller particles. The small particles of bean dregs were sieved. The portion under 140 meshes was collected for tests. The particle size is in the range of 0.090 mm and 0.106 mm. The proximate analysis of bean dregs was carried out according to ASTM standard. In this work, we calculated HHV for bean dregs including C, H, O and N based on Francis and Lloyd method (Cordero et al., 2001). The ultimate sample analysis was carried out using a VARIO EL111 elemental analyzer. The analysis results are presented in Table 1.

The contents of crude protein, crude fat, and crude cellulose were determined by the Kjeldehl method, the Soxhlet extract method, and the intermediate filtration method respectively. The analysis results are shown in Table 2.

2.2. In situ observational technique

In this study, bean dregs pyrolysis has been visualized directly using a capillary technique. A quartz capillary approximately 1.5 cm in length was flame sealed at one end using an oxyhydrogen flame machine. The inner and outer diameters of the capillary are 300 and 665 μm respectively. Approximately 0.1 mg of bean dregs was filled into the capillary, and then the other end of capillary was flame sealed. The capillary was inserted in a sample holder equipped in the hot and cold plate (HCP) which was connected to a temperature controller (INSTEC). The sample holder has a sample slot (1 mm wide, 2.5 mm deep, and 40 mm long) located at the middle part of the HCP. The schematic diagram of the in situ observation system and the pictures of the instrument are shown in Fig. 1. Image of sample was observed by a microscope and transferred to a computer through a CCD camera. Temperature was displayed and controlled by an intelligent digital control instrument. The heating rate adopted in the test for the in situ visualization was 30 °C/min.

2.3. Thermogravimetric analysis

The experiments were carried out in a STA 409 PC thermogravimetric analyzer (manufactured by Netzsch in Germany). In each experiment, approximately 7.3 mg of bean dregs were spread uniformly on the bottom of the ceramic crucible of the thermal analyzer. The pyrolysis experiments were performed at heating rates of 10, 30, and 50 °C/min in a dynamic high purity nitrogen flow of 20 ml/min. The temperature of the furnace was programmed to rise from room temperature to 800 °C.

Table 2
The chemical content analysis results of bean dregs (on dry basis).

Crude cellulose (%)	Crude protein (%)	Crude fat (%)
52.6	20.5	12.5

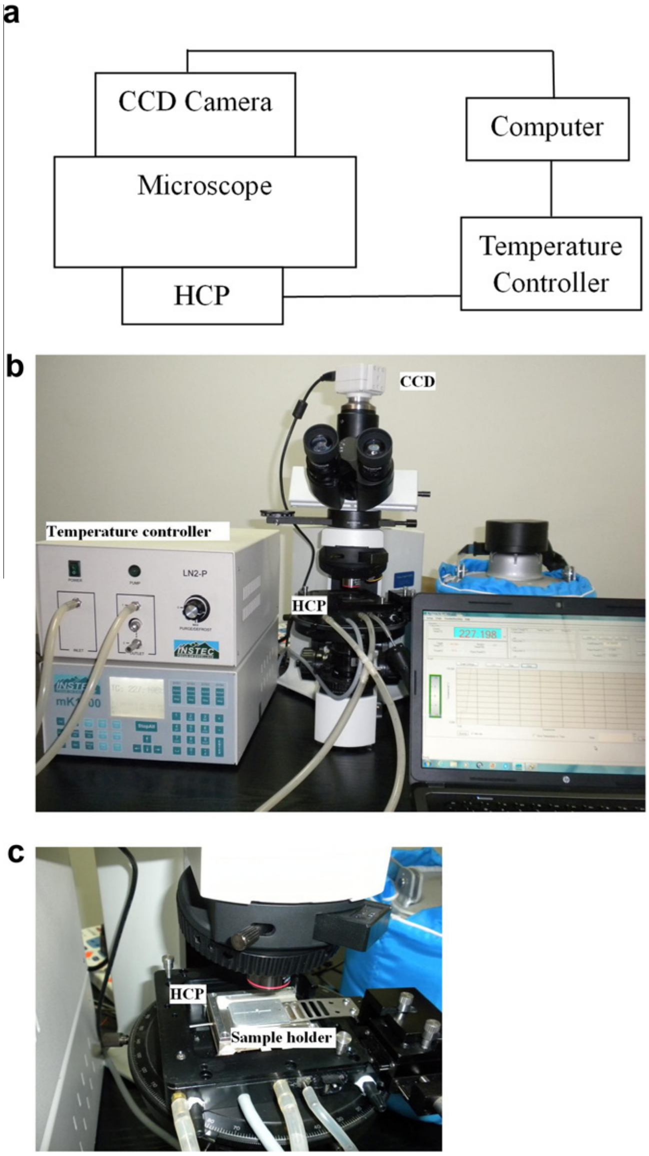


Fig. 1. Schematic diagram and pictures of the visualization system (a) Schematic diagram, (b) pictures of the instruments, (c) sample holder.

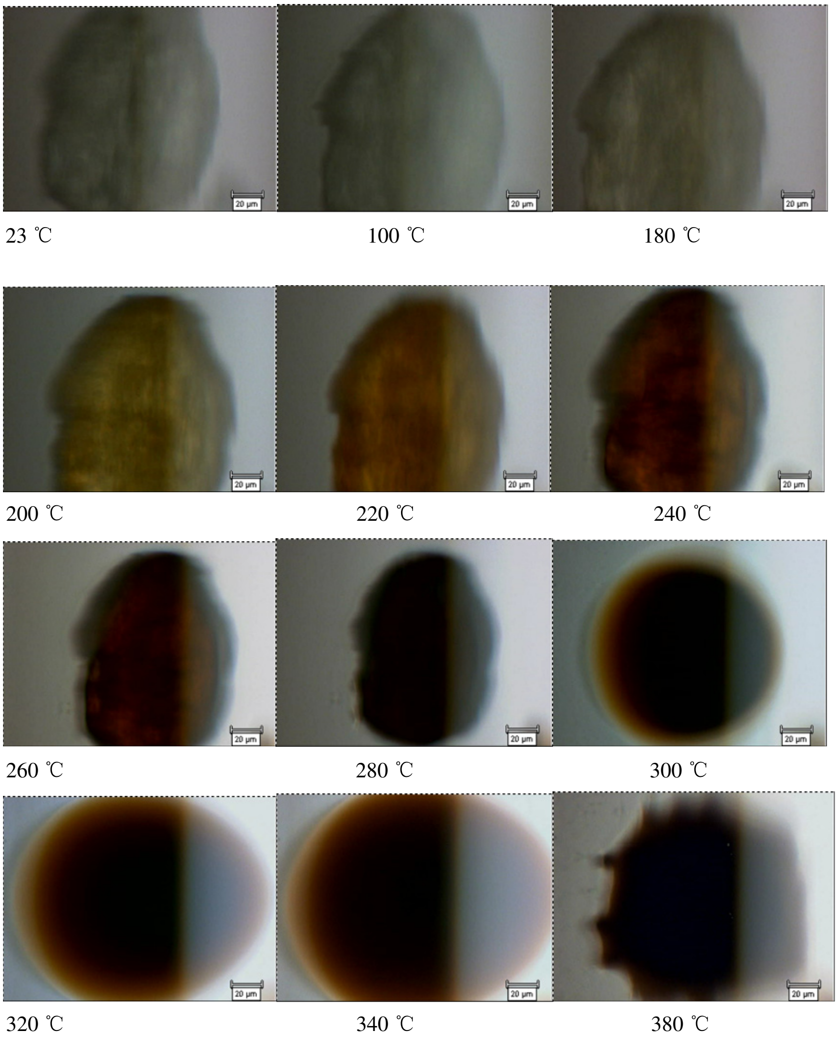
3. Results and discussion

3.1. In situ visualization of bean dregs pyrolysis transformation

Some micro-photographs showing transformations of bean dregs at different temperatures are given in Fig. 2.

Table 1
Sample characteristics of bean dregs.

Sample	Moisture (%)	Ash (%)	C (%)	H (%)	N (%)	O (%)	HHV (MJ kg^{-1})
Bean dregs	5.93	3.70	46.00	6.667	3.634	43.699	15.92


23 ℃ 100 ℃ 180 ℃

200 ℃ 220 ℃ 240 ℃

260 ℃ 280 ℃ 300 ℃

320 ℃ 340 ℃ 380 ℃

Fig. 2. Selected micro-photographs showing the pyrolysis transformation with increasing temperature of bean dregs.

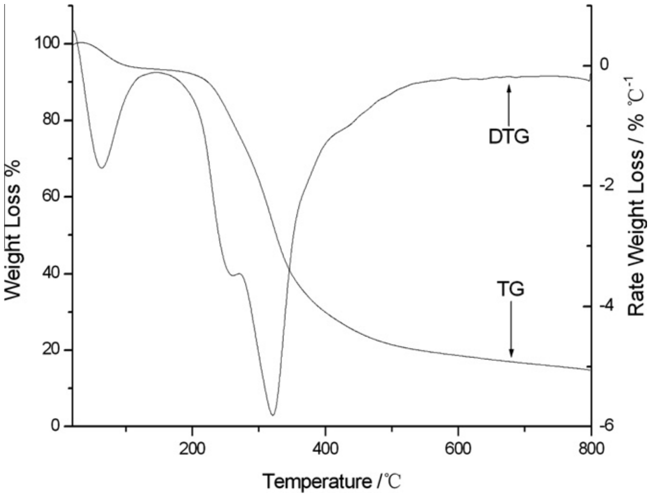


Fig. 3. Typical TG–DTG curves of bean dregs at a heating rate of 10 °C/min.

A series of in situ microscopic images in Fig. 2 show bean dregs transformation in quartz capillary. The appearance of bean dregs was retained up to 100 °C without noticeable changes. This indicates that chemical change of bean dregs did not occur in the temperature range of 23–100 °C. But in this stage, moisture was evaporated from bean dregs. The thermogravimetric (TG) and derivative thermogravimetric (DTG) analysis discussed later in the paper confirm the results. A small peak at 63.7 °C in the DTG curve (Fig. 3) is attributed to vaporization of moisture.

The color of bean dregs became pale yellow at 180 °C. The chemical reaction of bean dregs commenced at this temperature. Cellulose and protein are two main components of bean dregs (Zhu et al., 2010a,b, 2011). Because Cellulose is stable and the color of cellulose is retained up to 200 °C without noticeable change (Zhu et al., 2012), the color changes may be caused by the reaction of protein component of bean dregs.

Bean dregs gradually became darker from 180 to 240 °C. At temperature of 220 °C, the color change of cellulose component of bean dregs commenced (Zhu et al., 2012). At the temperature of 240 °C, orange oily liquid formed from the surface of solid bean dregs. At this temperature, both protein and cellulose decomposed. The breaking of the peptide bonds in the protein releases nucleophilic amines (Mullen and Boateng, 2011). Water and oily liquids are also produced from cellulose at this temperature (Zhu et al., 2012). With increasing temperature, the solid bean dregs continuously transformed slowly to oily liquid. At 260 °C, more oily liquids could be observed. This may be caused by the pyrolysis of protein component of bean dregs. A shoulder peak at 261.4 °C appeared as shown in Fig. 3. The shoulder peak was due to the decomposition of protein. With increasing temperature, some of the oily liquids evaporated. At the temperature of 280 °C, bean dregs became smaller and brown solids could be found. When temperature reached 300 °C, oily liquid was generated more quickly than before. A growing number of oil droplets formed a liquid spherule. The maximum rate of oily liquid production was observed at 320 °C. This is consistent with the result of TGA (Fig. 3). There is strong peak at 321.0 °C implying that decomposing rate of cellulose reaches its maximum value at 321.0 °C. The in situ observation experiment was carried out in a sealed quartz capillary. The TGA experiment was performed in a thermogravimetric analyzer with a high purity nitrogen flow of 20 ml/min. Because the two experiment methods are different, slight difference may exist in the experiment data obtained by the two methods. At the temperature of 340 °C, the liquid spherule attains the maximum. At the highest temperature of 380 °C of the experiment, the oily liquid became a viscous tarry lump and there was still a black solid residue. The residue may be char and undecomposed bean dregs.

In the liquefaction process, the main component cellulose was degraded to smaller compounds by dehydration, dehydrogenation, deoxygenation and decarboxylation. These compounds once produced, rearrange through condensation, cyclization and polymerization, leading to new compounds. The liquid fraction may consist of acetaldehyde, propion aldehyde, levoglucosan, butyraldehyde, acrolein, crotonaldehyde, furan, acetone, butanedione, methanol, methyl glyoxal, acetal, aromatics, phenols, and water (Demirbas, 2000; Zhong and Wei, 2004; Wang et al., 2007). Pyrolysis of soybean cake was investigated by Uzun et al. (2006). Pyrolysis oil consisted of 52.5% pentane solubles and 47.5% asphaltenes. Phenols, alcohols, ketones, aldehydes, alkenes, aromatics, carboxylic acids and derivatives were determined in the pyrolysis oil. Calorific values of bio-oil and char produced in the pyrolysis process were 23.30 and 18.26 MJ/kg respectively.

Bean dregs have a high protein content which is about 20 wt.% of bean dregs (Zhu et al., 2010b). The pyrolysis oils produced from the proteinaceous biomass have been shown to have several favorable characteristics when compared with pyrolysis oils from lignocellulosic biomass (Mullen and Boateng, 2011). The decreased oxygen content, decreased acidity, increased energy content, and in some case, greater stability make these pyrolysis oils more desirable for direct use as fuel, in a boiler for example. In the pyrolysis, bean dregs are converted to liquids, gases and char. Pyrolysis of bean dregs is a potential candidate for power production. It is a useful method of using waste biomass for energy production. Bioenergy production and utilization exhibited several positive impacts such as the reduction of quantity of wastes, reduced the emission of greenhouse gases by fossil fuel substitution (Budzianowski, 2011).

3.2. Thermogravimetric experiments

3.2.1. Thermal degradation process

Fig. 3 shows the weight loss and the rate of weight loss curve obtained during the pyrolysis of bean dregs sample under inert atmosphere at a heating rate of 10 °C/min. During thermal degradation of bean dregs, three stages can be distinguished during the heating process of the samples.

The first stage goes from room temperature to 246.5 °C; a slight weight loss in the weight loss curve is observed. This could be due to the loss of water and light volatile compounds. There was a small peak in the rate of weight loss curve, with a peak temperature at 63.7 °C. The small change of conversion in the sample was attributed to vaporization of moisture. The early minor weight loss in the bean dregs was attributed to desorption of moisture as bound water on the surface and the pores of bean dregs. As shown in Fig. 2, the appearance of bean dregs was retained in the temperature range from 23 to 100 °C without noticeable changes. From Fig. 3, we can see that 5.9% of moisture disappeared at 100 °C. The weight losses of the blend are very close to those from the linear superposition of the individual components (Chen and Kuo, 2011). Cellulose and protein are main components of bean dregs. Because cellulose is stable up to 200 °C (Zhu et al., 2012), protein component of bean dregs decomposed firstly in the first stage. As shown in Fig. 2, the color change of bean dregs at 180 °C was caused by protein. The light volatile compounds in the temperature range from 100 to 180 °C may come from pyrolysis of protein and moisture.

Table 3
Characteristic devolatilization temperatures and total volatile matter content for bean dregs, obtained at different heating rates.

Heating rate (°C/min)	T_s (°C)[a]	T_{max} (°C)[b]	$(dw/dt)_{\max}$ (% min^{-1})	VM (%)[c]
10	246.5	321.0	5.81	63.24
30	257.6	335.4	15.57	59.14
50	261.3	339.1	26.89	64.14

[a] T_s is the temperature of initial decomposition.
[b] T_{max} was determined from the respective DTG curve peaks.
[c] VM is the total volatile matter evolved in the second stage.

The second stage goes from 246.5 °C to 368.7 °C. The second stage was characterized by a major weight loss, which corresponded to the main pyrolysis process. Most of the organic materials were decomposed in this stage. The mass loss of this stage is more than 60% of total volatiles. In this stage, the bean dregs were liquefied as shown in Fig. 2. A shoulder peak in the DTG curve appeared at 261.4 °C in Fig. 3. The small shoulder was due to the decomposition of protein. Chicken feather fibers (CFFs) are mainly composed of crude fibers and proteins. The TG–DTG plot of bean dregs was similar to that of CFF. But the temperature ranges of the stages of CFF were different from those of bean dregs (Senoz et al., 2012). A strong peak appeared at 321.0 °C in the DTG curve. At this temperature, the rate of weight loss attained maximum. The main strong peak was due to the decomposition of cellulose. At the end of the second stage, about 62.3% of bean dregs were pyrolyzed.

The third stage goes from 368.7 °C to the final temperature (800 °C). In the third stage, the carbonaceous matters in the solid residuals continuously decomposed at a very slow rate. A slight continued loss of weight was shown in the weight loss curve. The residue yield of bean dregs was 17.9%.

The analysis of the rate of weight loss curve shows that only one strong peak was observed during the main pyrolysis process. This strong peak was due to the degradation of crude cellulose. The degradation characteristics of the bean dregs were given in Table 3.

3.2.2. Effect of heating rate

Fig. 4 shows the weight loss and the rate of weight loss curves obtained from the pyrolysis of bean dregs at different heating rates (10, 30 and 50 °C/min). All the curves contained a strong peak, which was attributed to the primary pyrolysis of cellulose. The peak shifted towards higher temperature with an increase in heating rate. A shoulder peak at a lower temperature was observed from the DTG curves, which also shifted towards higher temperature with the increase in heating rate. The shoulder peak was attributed to pyrolysis of protein. The general shift to higher temperatures occurs when the heating rate is increased. This is typical for all non-isothermal experiments. The main reason for these shifts is that bean dregs are a poor conductor of heat. There exists a temperature gradient throughout the cross-section of the bean dregs. At lower heating rate, the temperature profile along the cross-section can be assumed linear as both the outer surface and the inner core of the bean dregs attains same temperature at a particular time as sufficient time is given for heating. On the other hand, at a higher heating rate, a substantial difference in

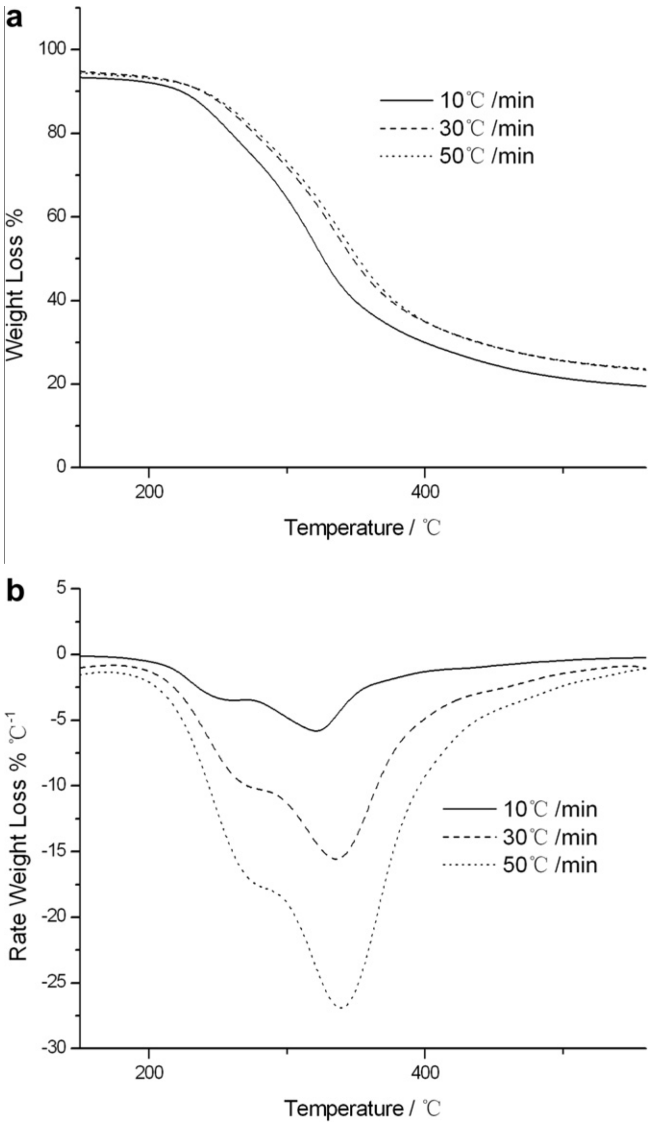


Fig. 4. (a) TG curves of bean dregs in different heating rate against temperature and (b) DTG curves of bean dregs in different heating rate against temperature.

temperature profile exists along the cross-section of the biomass (Maiti et al., 2007). The other reason may be due to the effect of heating rate on secondary reactions of the primary pyrolysis products (tar and high-molecular-weight compounds), as some authors have reported (Juntgen, 1984; Zou et al., 2010).

3.3. Kinetic parameters of bean dregs

In view of the fact that bean dregs are mixtures which are mainly composed of cellulose, protein and fat, the decomposition of bean dregs comprises a large number of reactions in parallel and in series, whereas DTG measures the overall weight loss rate. DTG, therefore, provides general information on the overall kinetics rather than individual reactions.

The analysis of TGA graphs was used to determine the kinetic parameters of bean dregs such as activation energy and Arrhenius frequency. The Coats–Redfern method (Coats and Redfern, 1964), Kissinger–Akahira–Sunose method (Kissinger, 1957), and the Flynn–Wall–Ozawa method (Flynn and Wall, 1966; Ozawa, 1965) were used to determine the pyrolysis kinetic parameters from the thermogravimetric data.

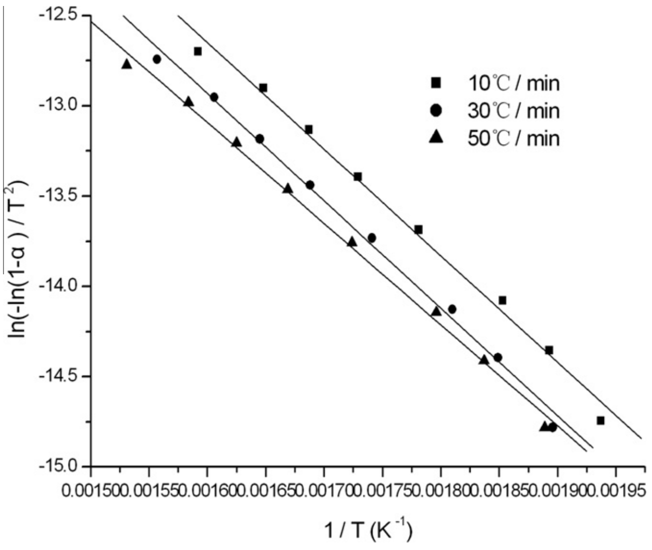


Fig. 5. Plots for determination of activation energy and the pre-exponential factor by Coats–Redfern method.

In the non-isothermal experiments carried out with a thermo balance, the sample mass was measured as a function of temperature. The rate of degradation or conversion, $d\alpha/dt$, is a linear function of a temperature-dependent rata constant, k and a function of conversion, $f(\alpha)$. The rate of conversion is expressed as,

$$\frac{d\alpha}{dt}=kf(\alpha) \tag{1}$$

where α is the converted rate of reaction, which is defined as $(w_0-w)/(w_0-w_\infty)$, t is the time, w_0 is the mass of initial sample, w is the mass of actual sample at time t, w_∞ is the mass of residue at the end of the reaction, and k is the rate constant, which is also defined by the Arrhenius equation:

$$k=A\exp\left(-\frac{E}{RT}\right) \tag{2}$$

where A is the pre-exponential factor, E is the activation energy, R is the gas constant, and T is the absolute temperature.

For a linear heating rate of, say, β Kelvin·min^{-1}:

$$\beta=dT/dt \tag{3}$$

By combining Eqs. (1)–(3), the reaction rate can be written in the form:

$$\frac{d\alpha}{f(\alpha)}=\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)dT \tag{4}$$

The integrated form of Eq. (4) is generally expressed as

$$G(\alpha)=\int_0^\alpha\frac{d\alpha}{f(\alpha)}=\frac{A}{\beta}\int_{T_0}^{T}\exp\left(\frac{-E}{RT}\right)dT=\frac{AE}{\beta R}P\left(\frac{E}{RT}\right) \tag{5}$$

where $G(\alpha)$ is the integrated form of the conversion dependence function $f(\alpha)$. Essentially the technique assumes that the A, $f(\alpha)$ and E are independent of T while A and E are independent of α, then Eq. (5) may be integrated to give the following equation in logarithmic form:

$$\ln G(\alpha)=\ln\left(\frac{AE}{R}\right)-\ln\beta+\ln P\left(\frac{E}{RT}\right) \tag{6}$$

Based on these equations, different kinetic methods were applied in this study.

3.3.1. Coats–Redfern method

Coats–Redfern method is an integral method, and it involves the thermal degradation mechanism. Using an asymptotic approximation for the resolution of Eq. (6) ($2RT/E \ll 1$), the following equations can be obtained:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (\text{for } n\neq 1) \tag{7}$$

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (\text{for } n = 1) \tag{8}$$

where n is the order of reaction.

Thus a plot of either $\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ against $1/T$ or, where $n = 1$, $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ against $1/T$ should result in a straight line of slope $-E/R$ for correct value of n. From the slope of the line, we can estimate apparent activation energy. If $2RT/E \ll 1$, we can estimate the pre-exponential factor from the intercept of the line. Many researchers (Lu et al., 2009; Sorum et al., 2001) assumed that devolatilization in the kinetic analysis of DTG data was a first-order reaction for the biomass wastes. Therefore, the pyrolysis of bean dregs was seen as a first-order reaction. We can draw a plot of $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ against $1/T$ to estimate the apparent activation energy pre-exponential factor of bean dregs pyrolysis. These plots resulted in straight lines (Fig. 5). From Fig. 5, we can see the relationship between $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ and $1/T$. The values of activation energy and pre-exponential factor calculated by Coats–Redfern method are given in Table 4.It can be seen from Table 4 that the activation energies of the bean dregs are in the range of 46.58–49.43 kJ/mol. As shown in Fig. 5, there is a good linear relationship between $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ and $1/T$ at different α ranging from 10% to 70%. All the plots have a high linear correlation coefficients greater than 0.99, so the assumption on a first-order reaction is feasible.

3.3.2. Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO) methods

The KAS method is based on the Coats–Redfern approximation (Coats and Redfern, 1964). It follows that:

$$P\left(\frac{E}{RT}\right) \approx \frac{\exp(-E/RT)}{(E/RT)^2} \tag{9}$$

From relationships (6) and (9) it follows that:

$$\ln\frac{\beta}{T^2} = \ln\frac{AR}{EG(\alpha)} - \frac{E}{RT} \tag{10}$$

Thus, the plot $\ln(\beta/T^2)$ versus $1/T$ for a constant value of α should be a straight line whose slope can be used to evaluate the activation energy.

The FWO method is derived from integral isoconversional method. Using Doyle's approximation (Doyle, 1961; Aboulkas et al., 2010) for the integral which allows ($\ln P(E/RT) \approx -5.331 - 1.052\,(E/RT)$), Eq. (6) can be simplified as

$$\ln\beta = \ln\frac{AE}{RG(\alpha)} - 5.331 - 1.052\frac{E}{RT} \tag{11}$$

Thus, for α = constant, the plot $\ln\beta$ versus $1/T$, obtained from thermograms recorded at several heating rates, should be a straight line whose slope can be used to evaluate the activation energy.

Compared with the Coats–Redfern method, the KAS method and the FWO method have the advantage that they do not require previous knowledge of the reaction mechanism for determining the activation energy.

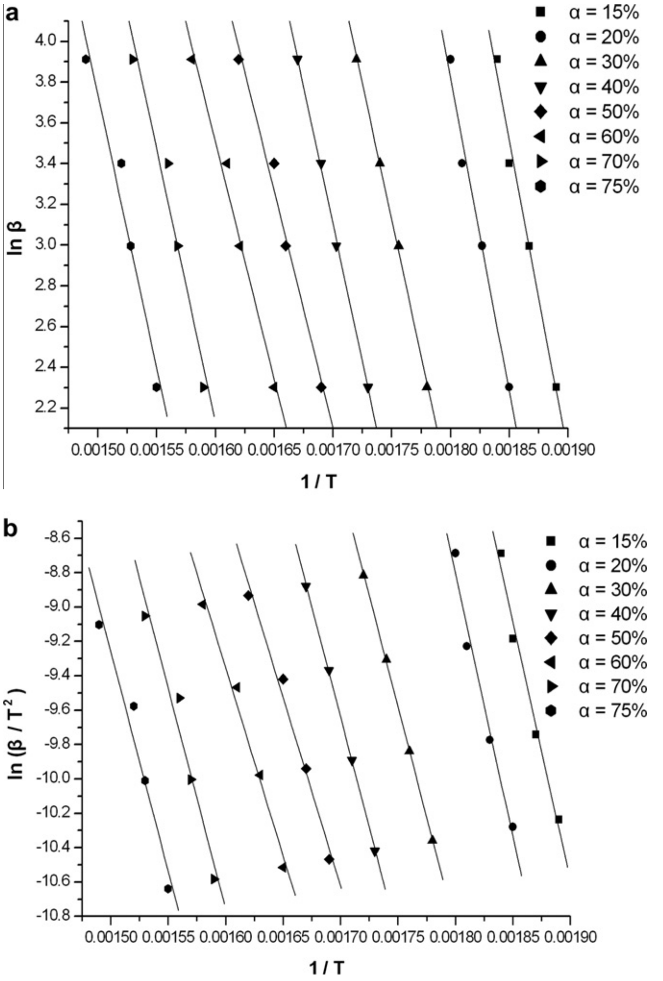


Fig. 6. (a) Plots for determination of activation energy at different α by FWO method and (b) plots for determination of activation energy at different α by KAS method.

Table 4
Results of bean dregs pyrolysis kinetic with Coats–Redfern method.

Heating rate β (°C/min)	T (°C)	α (%)	E (kJ/mol)	A (s^{-1})	R
10	243.1–355.2	10–70	48.98	2342	−0.9961
30	254.4–368.9	10–70	49.43	5847	−0.9976
50	256.3–380.0	10–70	46.58	4519	−0.9980

According to Eqs. (10) and (11), a plot of $\ln(\beta/T^2)$ against $1/T$ or $\ln\beta$ against $1/T$ should be a straight line. These plots resulted in straight lines as shown in Fig. 6. From the slope of line in Fig. 6, we can estimate apparent activation energy of the bean dregs degradation at various conversion α. Fig. 6 shows the representative plots for the main stage of weight loss (i.e., the second stage). According to Fig. 6, the activation energies calculated by the KAS and FWO methods are listed in Table 5.

As shown in Table 5, all plots, except α = 75%, had fairly high linear correlation coefficients greater than 0.99, and the average values of activation energy worked out by the KAS and FWO methods vary slightly. The activation energies slightly varied with the degree of conversion, indicating that there exists a high probability for the presence of a single-step reaction (Vyazovkin, 2000). It can be seen from Tables 4 and 5 that the activation energies of the bean dregs were in the range of 199.9–231.8 kJ/mol (by KAS method) and 199.8–230.8 kJ/mol (by FWO method) at different

Table 5
The activation energies obtained by KAS and FWO method.

Conversion rate (α %)	KAS method		FWO method	
	E (kJ/mol)	R	E (kJ/mol)	R
15	223.4	−0.9954	221.1	−0.9958
20	225.4	−0.9948	218.1	−0.9970
30	224.0	−0.9998	222.1	−0.9998
40	213.2	−1.0000	212.0	−1.0000
50	206.0	−1.0000	205.4	−1.0000
60	199.9	−0.9995	199.8	−0.9996
70	211.0	−0.9917	210.7	−0.9925
75	231.8	−0.9740	230.8	−0.9763
Average	216.8		215.0	

conversions. It is interesting to compare the kinetic activation energy values obtained by KAS and FWO methods with those calculated by Coats–Redfern method. The activation energy values calculated by KAS and FWO method are larger than those calculated by the Coats–Redfern method. The activation energy obtained by Coats–Redfern method ranges from 46.58 kJ/mol to 49.43 kJ/mol. This phenomenon is consistent with the results of the previous literatures and may be caused by the assumptions of different kinetic methods (Shih and Jeng, 2006; Shih, 2005; Song et al., 2003).

4. Conclusions

The paper deals with the pyrolysis of bean dregs by an in situ visualization technology and a thermogravimetric analyzer to investigate the thermal degradation characteristics of bean dregs. Oily liquids were produced during bean dregs pyrolysis in a quartz capillary. In situ visualization of reaction enables us to observe bean dregs transformation during pyrolysis. The color change of bean dregs during pyrolysis occurred at 180 °C and was caused by the reaction of protein component of bean dregs. Oily liquid production was observed at 240 °C. Both cellulose and protein were liquefied at this temperature. The maximum rate of oily liquids production was observed at 320 °C.

TGA of bean dregs suggests that there were three distinct stages of weight loss. The first stage ranged from room temperature to 246.5 °C, the second stage from 246.5 °C to 368.7 °C and the third stage from 368.7 °C to the final temperature (800 °C). The second stage is the main pyrolysis process and most of the organic materials are decomposed in this stage. The kinetic parameters were obtained by Coats–Redfern, KAS and FWO methods. The average values of activation energy by the three methods are 48.3, 216.8 and 215.0 kJ/mol respectively.

It has been shown that visualization of bean dregs pyrolysis in a quartz capillary has the potential to reveal many important processes occurring during bean dregs transformation which are not recognized using conventional pyrolysis techniques. The generation processes of oily liquid can be observed directly. In situ visualization technique has potential application to biomass pyrolysis. In the pyrolysis, bean dregs are converted to liquids, gases and char. Bean dregs are potential feedstock for energy production.

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